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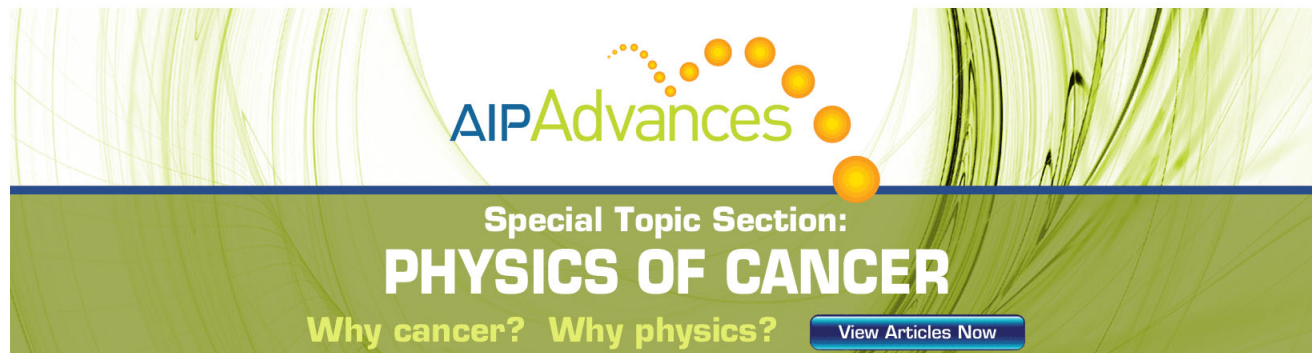
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Electronic properties of individual diarylethene molecules studied using scanning tunneling spectroscopy

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The investigation of the electronic conduction through monosulfurdiarylethene (1S-DE) immobilized in an insulating dodecanethiol matrix on a gold surface was addressed. Scanning tunneling spectroscopy allows to probe spatially the frontier molecular orbitals of 1S-DE at 77 K. We locally extracted the electronic highest occupied molecular orbital-lowest unoccupied molecular orbital gap of 1S-DE with the value of 1.56 eV. This attempt reveals the importance of scanning tunneling spectroscopy as a tool to measure the charge transport properties of diarylethene towards the realization of a switching-based molecular device. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4706568>]

I. INTRODUCTION

The use of single organic molecules as building blocks of electronic devices is potentially promising for technological applications.^{1–4} Various reports have shown that a molecule bearing a functionality can constitute a basis for a single molecule device.^{5–9} One aspect that needs consideration is the nature of the electron transport through the molecules. Self-assembled monolayer films (SAMs) of long-chain alkylthiol molecules have been extensively studied due to the ease with which they form an ordered nanostructure especially on gold substrates.^{10,11}

Scanning tunneling spectroscopy (STS), with its high precision and stability, is a powerful tool in determining the local electronic properties of a single molecule. At glance, a typical STS experiment can be considered as a vertical two-probe geometry, measuring the variation of the tunneling current through a single molecule as a function of bias voltages. STS determines quantitatively the position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of single molecule with high spatial precision.

Diarylethene molecular switches have been considered to hold a great promise in the progress of molecular devices. Features such as its molecular rigidity, high fatigue resistance, and excellent addressability^{12,13} have led to much interest in the development of electronic devices with these switches. When a diarylethene absorbs light, a transition from the ground state to an excited state occurs and a photochemical reaction from the so-called “on” state to the “off”

state occurs (or *vice versa*). The closing or opening of a diarylethene covalently bound to gold surface can be controlled reversibly via light irradiation using distinct wavelengths.¹⁶ In addition, the “off” and “on” states of diarylethenes incorporated between two gold electrodes exhibit different charge transport properties.¹⁸

Despite the growing interest in diarylethene photochromic switches as opto-electronic molecular components, there have been no experimental investigations of electronic structure with regard to their charge transport properties. The versatility of STM as a surface tool and as a local probe of electronic properties of individual molecules can provide new insight into electronic properties of immobilized thiol-based diarylethene within the alkylthiol matrix on gold.¹⁷

We report on the successful investigation of the presence of a single diarylethene molecule [monosulfurdiarylethene (1S-DE) on a gold surface as illustrated in Figure 1. Moreover, we present quantitative findings which show distinctive features between the “on” state of diarylethene versus dodecanethiol (DT) molecules by comparing their respective tunneling conductance (dI/dV) and tunneling current (I) versus bias voltages at 77 K. It would be of interest to measure the charge transport properties of the “off” state. However, it remains a challenge to unambiguously differentiate between the “off” state of diarylethenes and surrounding DT molecules owing to their comparable apparent heights.¹⁶ Hence, the current studies are restricted to the investigation of the “on” state of 1S-DE.

II. EXPERIMENTAL SECTION

The chemical synthesis of 1S-DE is described elsewhere.¹⁴ Self-assembly procedures were performed based on earlier reports.^{2,16} Metal substrates consisting of a 150-nm

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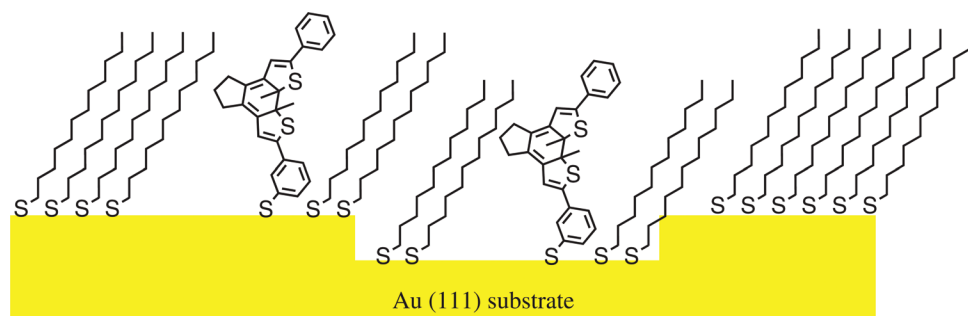


FIG. 1. An illustration of the molecular confinement of 1S-DE molecule between DT matrix.

thick layer of gold deposited on mica was used. Prior to self-assembly, STM analysis confirmed the presence of an atomically flat Au(111) terraces. Then, the gold substrate was immersed in a 1.5 mM of DT in ethanol for 12 h. To clean the unused DT on surface, the substrate was introduced into pure ethanol solution for three times and dried under a nitrogen flow. Subsequently, the gold substrate was immersed in a 0.5 mM of 1S-DE ethanolic solution for 6 h. Finally, the substrate was again washed with ethanol as described above. Constant current STM images were acquired using PicoLE STM setup (Agilent) with a final preamplifier sensitivity of 1 nA/V was used for STM measurements. The topography of the samples was acquired using mechanically cut Pt/Ir tips for ambient experiments and an electrochemically etched tungsten tip for the liquid nitrogen experiment. Initially, the sample was inspected in ambient condition, before the sample was transferred to the UHV chamber for further charge transport experiments. The measurements discussed here were carried out in the ultra-high vacuum low-temperature STM operated at 77 K and base pressure of 1.5×10^{-10} mbar. Si-

multaneous tunneling current and differential conductance versus bias voltage were collected using lock-in technique. The bias range was swept over 1.5 V, and a single sweeping trace was collected in 0.01 s.

III. RESULTS AND DISCUSSION

In Fig. 2(a), a high yield of randomly distributed 1S-DE molecules is typically observed over the entire of the gold sample. 1S-DE molecules represented as bright spots can be found at the near step edges (known as favorable sites of missing DT molecules). Statistically, the surface coverage of 1S-DE molecules on gold is calculated 0.7% (based on the spot analysis using Gwyddion version 2.90). In addition, the mean grain area is obtained with a value of 2.14 nm^2 . This value is in agreement to the typical dimension of single diarylethene found elsewhere.¹⁵

The lateral profiles correspond to the two respective cross sections in Fig. 2(c) indicated that the presence of 1S-DE single molecule was clearly resolved. Typically,

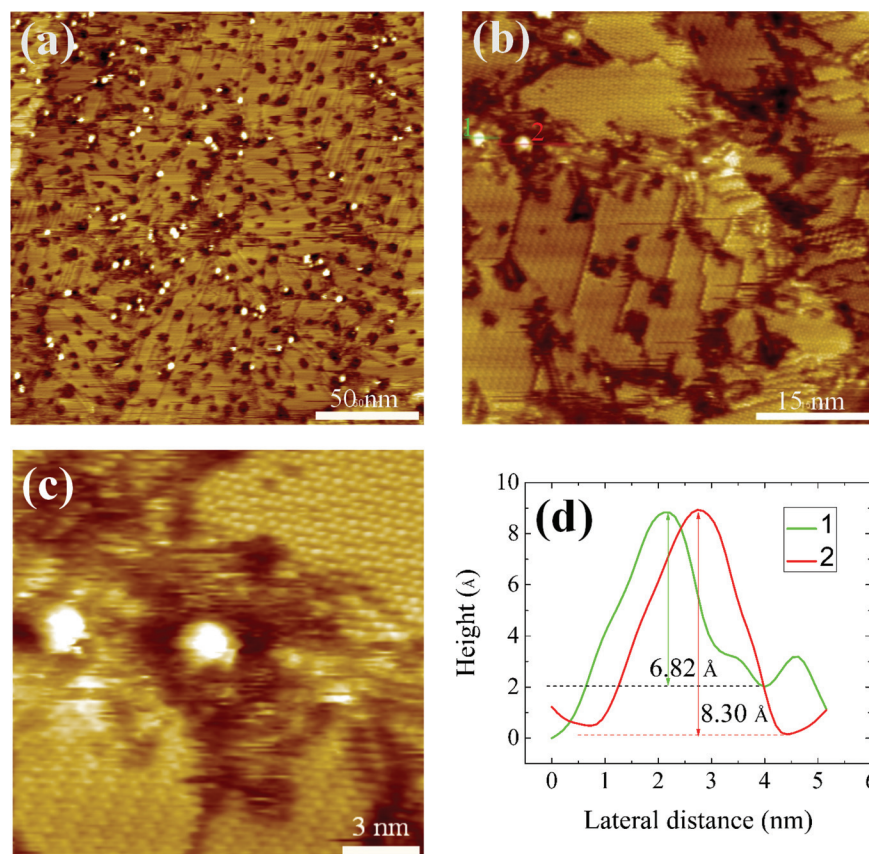


FIG. 2. Constant current STM images showing the mixed m-DE and DT monolayers in a large scale acquired at room temperature. (a) Large scan area showing a high yield population of 1S-DE molecules (scan image: $200 \times 200 \text{ nm}^2$; $I_t = 30 \text{ pA}$; $V_{bias} = 800 \text{ mV}$). (b) High resolution image showing the presence of two 1S-DE molecules as bright spots surrounded by DT domain boundaries. (c) An observation of the hexagonal (top-right corner) and the square lattice (bottom-left corner) of DT at the vicinity of the two 1S-DE. (d) Cross-sections of the bright protrusions (Fig. 1(b)) show typical widths and apparent heights of two individual 1S-DE molecules.

1 S-DE signature appears as a bright spot in STM image with apparent heights above 4 Å with respect to the neighboring DT.¹⁶ Moreover, the diameter of the bright spots ranges from 2–3 nm (Fig. 2(d)) in agreement with the typical size of a single aromatic molecule previously observed by Donhauser and coworkers.¹⁵ 1S-DE molecules are usually found at boundaries of the DT domains or in the disordered areas and etch pits.

Charge transport properties of the "on" state of 1S-DE were investigated by collecting the tunneling conductance spectra at different locations. Initially, we locate a bright spot and nearby DT lattices in the topographic STM image. Then we move the tip on top of a bright spot and the feedback loop is temporally disabled at a fixed tip-sample distance (typically, the tunneling parameters are $I_t = 12$ pA and $V_{tip} = 1$ V). During this period, the variation of the tunneling current as a function of bias voltage on the bright spot is collected. The same

procedure is repeated for DT using the same tunneling conditions. STM inspection was employed in between the acquisition spectra in order to evaluate any possible lateral drift during measurements. The average of the I-V and the dI/dV spectra was obtained from hundred traces where ten of 1S-DE molecules contributed to the final curves.

In Figs. 3(a)–3(d), four consecutive single I-V traces were subsequently measured on top of DT (red curve) and a 1S-DE (black curve) molecule with the same initial tunneling setpoints. We note that the same bright spot was probed to acquire these measurements. Qualitatively, the shape of the I-V curves of the closed form of 1S-DE shows different feature compared to DT (Fig. 3(e)). These observations are more prominent when probing both molecules at a higher voltage (>1 V). No appreciable feature in the I-V of DT is detected due to its large electronic band gap (8 eV).¹⁹ For 1S-DE, several kinks were clearly observed in the I-V

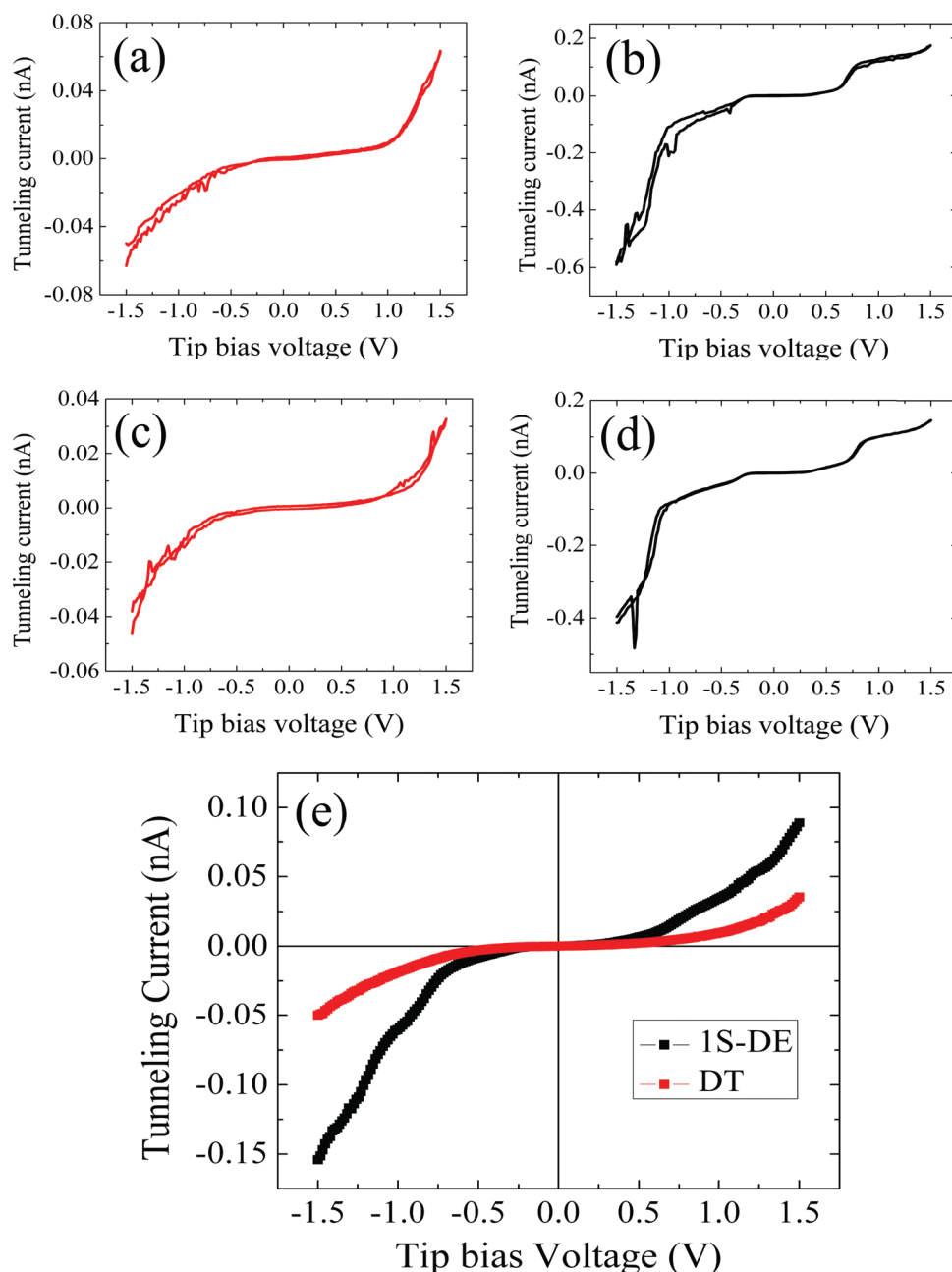


FIG. 3. The I-V characteristics of a 1S-DE and DT molecule. (a)–(d) Four consecutive individual I-V traces were collected in alternate fashion to acquire the molecular signature of 1S-DE (black curve) and DT (red curve). (e) The average I-V spectra taken from hundred traces which shows distinctive features especially presented in the 1S-DE curve.

characteristics at small bias voltages. For sake of clarity, we have performed the same procedure on a different location on the same sample, and we did not observe a significant variation in our result (see supplementary information).³⁷ The origin of this observation can be attributed to the increase (or decrease) of the tunneling current when the Fermi level (hereafter abbreviated as E_F) of the gold substrate or tungsten tip is resonantly aligned (or nonaligned) with the frontier molecular orbitals of 1S-DE.

Further analysis is focused on the I-V shape of the molecule of interest: 1S-DE. In Fig. 3(e), the I-V characteristics appear to be linear for small voltages,²⁰ while asymmetry sometimes is observed at higher voltages (approx. 1 V). The origin of the I-V asymmetry has been ascribed to various mechanisms: Coulomb blockade,^{21,22} geometric asymmetry of the molecular junction,^{23–25} or the involvement of molecular orbitals.²⁶ The I-V asymmetry is also a fundamental feature related to a rectifying behaviour,^{27,28} which deserves some attention in the interpretation of the I-V characteristics of 1S-DE versus those of DT. Let us discuss each aspect separately between two cases in order to unravel the relevant factors contributing to asymmetry of the I-V curves. Coulomb blockade can be ruled out since we did not observe

any symmetric regular step-like features in the IV-curves of both molecules in Figures 3(b) and 3(d). Rectification behavior was also absent in the I-Vs of both molecules. We consider a strong coupling of the molecule with the substrate and a weak coupling of the molecule with the tip. This is a common assumption for chemisorbed molecules in STM-based molecular junctions. The position of the energy levels is therefore fixed relative to the Fermi energy of the metallic substrate. As a consequence, one will measure the energy position of the molecular orbitals with respect to the metal by means of dI/dV measurements. The position of the energy levels (HOMO and LUMO) does not have to be symmetric around the Fermi energy of the metal, which is consistent with the measurements. The found asymmetry of the average I-V curves of 1S-DE (Fig. 3(e)) should originate from the involvement of orbitals as other effects have been ruled out. This asymmetry is particularly visible at a high bias voltage (1.5 V); the tunneling current ratio of the positive and negative regions obtained was approximately 1.5.

Simultaneous dI/dV spectra of 1S-DE and DT were recorded (Figs. 4(a) and 4(b)). These individual traces show the different features of dI/dV signal in each case. In a similar manner as the I-V spectra previously described in Fig. 3(a),

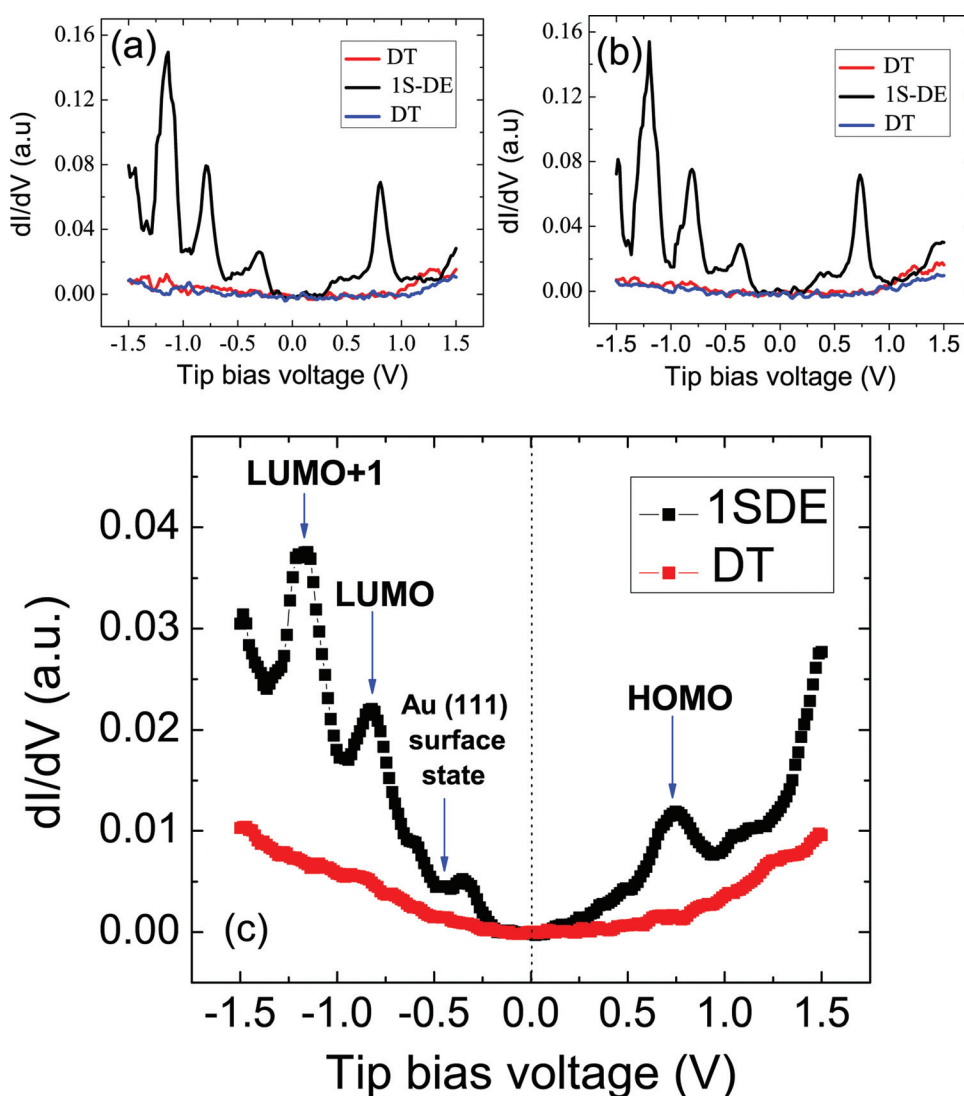


FIG. 4. A comparison of the dI/dV spectra of 1S-DE and DT on Au(111). (a) Individual traces of dI/dV signals taken subsequently on top of a different molecule. (b) The repetition of the dI/dV measurements acquired on the respective molecules as displayed in (a). (c) Averaged dI/dV spectra of 1S-DE (black line) and DT (red line) hundred individual traces of the tunneling conductances. The 1S-DE dI/dV spectrum shows three broad molecular and one gold surface states. The first occupied (HOMO) level is found in the positive regime with respect to the Fermi energy. In the negative regime (left part), two distinguishable tunneling resonances, LUMO and LUMO + 1 are found. For comparison, the dI/dV spectrum of DT does not show any features that could be assigned to molecular states.

consecutive dI/dV measurements were carried out on top of 1S-DE and DT, respectively. As expected, the molecular signatures are clearly observed in the dI/dV of 1S-DE, whereas a featureless dI/dV spectrum can be found for DT. A dip close to 505 meV was observed together with the 1S-DE features as shown in Fig. 4(c). This feature can be associated to the presence of Au(111) surfaces state according to Chen *et al.*³¹ A similar procedure was also implemented in the work of Nicoara *et al.*³² and Wegner *et al.*³³ In general, the higher conductance is expected to be found in the dI/dV of the 1S-DE in its "on" state since DT in nature is less conductive than 1S-DE. The evolution of the outmost frontier orbitals of 1S-DE is further discussed. Several differential conductance peaks were successfully resolved: -820 mV, -1170 mV and $+740$ mV as shown in Fig. 4(c).

Let us discuss the latter value, which corresponds to the contribution of the HOMO. In the negatively bias region, the first and the second unoccupied molecular orbitals were successfully resolved with the energy separation of 350 meV between these two broad peaks. Based on these results, we determine the HOMO-LUMO electronic gap of 1S-DE to be 1.56 eV. This attempt emphasizes that STS is powerful enough to discriminate individual frontier molecular energy levels with submolecular precision at 77 K.

To correlate our experimental findings, we compared several existing theoretical work on diarylethenes that had been carried out. Two research groups explored independently the switching properties of diarylethene molecular junctions.^{30,34} They reported that the transmission peak originates from the presence of the HOMO of the "on" state lying close to the E_F of the gold electrode. Further on our results are in agreement with the theoretical result described by Huang *et al.*³⁵ They have shown that a diarylethene molecular junction in the "on" state displays significant transmission peaks that are located below and above the E_F . The values are about -0.8 eV and 0.5 eV with respect to the E_F . These features are assigned to the perturbed HOMO and LUMO orbitals, respectively. It implies that the expected HOMO-LUMO gap of 1S-DE at the "on" state is 1.3 eV. Interestingly, this theoretical value is quite comparable to the extracted value of our STS experiment. Further, we compare our experimental result based on the relative position of each molecular orbital energy level with respect to the E_F ($V_{bias} = 0$). The closest lying molecular orbitals to E_F is expected to have the strongest contribution to the electron conduction across a molecule. Since the HOMO peak is found 0.74 eV above E_F (80 meV closer than the LUMO level), we propose that the charge transport properties of 1S-DE are dominated by the tail of the perturbed HOMO rather than the LUMO level at small bias voltage. We also notice that other experimental evidences coming from non-single molecule based junctions,^{28,29,34} displayed charge transport properties dominated by the transmission from the perturbed HOMO as in our case for single molecule junction.³⁶

IV. CONCLUSION

In summary, we were able to characterize the local electronic properties of the "on" state of 1S-DE diarylethene

molecule using STS measurements at low temperature. I-V spectra of 1S-DE and the surrounding DT matrix exhibited distinctively different features owing to the presence of the electronic states in the vicinity of the Fermi level of the former one. Moreover, the electronic gap between the HOMO and LUMO level was determined to be 1.56 eV. In addition, we proposed that the charge transport property of 1S-DE is most likely dominated by the perturbed HOMO level rather than the LUMO level.

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- ³⁷See supplementary material at <http://dx.doi.org/10.1063/1.4706568> for other evidence of the I-V and dI/dV curves of 1S-DE and DT molecule on a different location.